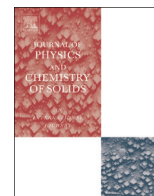




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Reduced humic acid nanosheets and its uses as nanofiller

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ABSTRACT

Leonardite is highly oxidized form of lignite coal and contains a number of carboxyl groups around the edges of a graphene-like core. A novel approach has been developed to synthesize graphene oxide-like nanosheets in large scale utilizing leonardite as a starting material. Humic acid extracted from leonardite has been reduced by performing a high pressure catalytic hydrogenation. The reaction was carried out inside a high pressure stirred reactor at 150 °C and 750 psi ($\sim 5.2 \times 10^6$ Pa). Morphology of the as-synthesized samples showed porous platy particles and EDAX analysis indicates the carbon and oxygen atomic ratios as 96:4–97:3%. The as-synthesized material has been used as nanofiller in polyurethane. The reduced humic acid–polyurethane nanocomposite showed over 250% increase of Young's modulus. This new approach provides a low cost and scalable source for graphene oxide-like nanosheets in nanocomposite applications.

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1. Introduction

Ten years ago, the two Russian scientists, Andre Geim and Constantin Novoselov, discovered the first free standing graphene sheet with the thickness of one carbon atom. During the intervening years, intensive work has been done to explore the properties of this extraordinary material [1]. The fact that graphene has extraordinary physical and chemical properties makes it promising in many diverse applications [2–4]. For example, graphene is considered as the strongest material ever discovered due to the in plane honeycomb structure. Even if graphene does not have the perfect crystalline structure, it still remains the strongest material ever known. It also possesses the highest electrical and thermal conductivities and has many promising applications [5–7].

The biggest challenge encountered by any new material is the ability to be produced in large scale at reasonable cost. This is the main problem encountered by carbon nanotubes which has only seen adoption in high end value added products. Nowadays there are many methods for the graphene synthesis. The first method was used in 2004 using the scotch tape to peel the graphene layers from the Highly Ordered Pyrolytic Graphite (HOPG). Although the scotch tape method is very simple and requires no

special equipment, it can be used only inside the laboratory and not suitable for industrial application. There are many methods that have been tried to produce graphene. For example, production of graphene by vacuum annealing of silicon carbide layer which is a quite expensive method that is difficult to transfer to any other substrates. Graphene synthesis using the Chemical Vapor Deposition (CVD) has been proposed by Ruoff group [8]. In this method, metal substrate (Cu or Ni) foils are heated at high temperature (over 1000 °C) in the presence of a mixture of carbon source gas (usually methane) and hydrogen. Although high quality large area graphene could be synthesized using this method, it is considered as an expensive method and not suitable for using graphene in nanocomposites. The most promising method for the graphene synthesis in large scale is the reduction of graphene oxide. In this method, graphite is oxidized with HNO₃ and H₂SO₄ after sonication and purification, graphene oxide will be produced which can be reduced using hydrogen or hydrazine [9]. This method consists of too many steps which affect the final cost of the product. Moreover, using hydrazine in the reduction of the graphene oxide is very dangerous and has environmental issues.

Humic acid could be obtained by acidification of the alkali extract of the organic matter. The color of the humic acid is brown and it is usually used in the soil to fix nitrogen for the plant nutrition [10]. Humic acid derived from leonardite is considered as low cost and readily available source of functionalized graphene platelets. Because these suspensions are black in color, we propose that they are highly conjugated and analogs of graphene. They

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contain carboxylic acid moieties that, as the black color would suggest, do not disturb the conjugation to a major degree and therefore must be primarily located at the edge of the sheet. These carboxylic acid groups, when converted to carboxylate ions by reaction with a base, impart water dispersibility to the particles.

In the present study, reduced humic acid from leonardite has been synthesized in large scale by the catalytic hydrogenation using the high pressure stirred reactor at low temperature (150 °C). Moreover, the feasibility of using reduced humic acid as nanofiller has been investigated.

2. Experimental work

Reduced humic acid preparation method was mentioned in details elsewhere [3], in brief, 3 g of leonardite was dissolved by 300 ml of double deionized water and using a 1 M KOH (or NH₄OH) solution under magnetic stirring, the pH was adjusted to 10. The solution was then filtered to remove any big particles or any residual impurities. The resulting humic acid dispersion was loaded into the bench top reactor and about 3 g of ruthenium catalyst was added. The reactor was flushed using ultra-high purity hydrogen until the pressure reached 200 psi for three times. The reactor was then pressurized with hydrogen to 520 psi. The temperature of the reactor was then increased from 25 °C to 150 °C over the course of 30 min, with stirring, reaching a pressure of approximately 750 psi ($\sim 5.2 \times 10^6$ Pa). The reactor was allowed to run for 24 h. After cooling, the resulting dispersion was filtered and collected. An ion exchange column was filled by ion exchange beads to a depth of 1 ft. The column was charged with 1 M HCl until the effluent was acidic to pH paper (pH \sim 4). The column was then flushed with diH₂O until the effluent was neutral to pH paper. The suspension was run through the ion exchange column and collected.

In order to prepare reduced humic acid–nanocomposite films, 200 g of the polyurethane (Bayhydrol 124) suspension was mixed by 200 g of the graphenol suspension. After sonication the mixture

was allowed to dry. After drying in Teflon[®] coated pan, the film was removed and placed on a glass sheet then placed in a convection oven at 70 °C overnight then the cutting die and press were used to stamp out specimens for tensile testing. This procedure was carried out three times to make three samples of reduced humic acid nanocomposite films.

In order to study the morphology of the samples, Helios Nanolab[™] 400 Dual Beam scanning electron microscope attached by energy-dispersive X-ray spectroscopy (EDAX) has been used. Atomic force microscope (AFM), Veeco Dimension 3100, in tapping mode was used in order to study the morphology and thickness of the graphenol. Raman spectroscopy system (Model Renishaw system 2000) with excitation Ar⁺ laser at wavelength of 488 nm with power of 100 mW has been used to investigate the vibration modes from reduced humic acid. Dynamic mechanical analysis (DMA), Q 800 from TA Instruments, has been used to study the mechanical properties of the graphenol nanocomposites; the film tension holder has been used. Transmission Electron Microscope, JEOL 1200 TEM, has been used to study the dispersion of the reduced humic acid nanosheets inside the polyurethane.

3. Results and discussions

3.1. Morphology

Fig. 1 contains SEM images of the spin-coated samples of reduced humic acid on a silicon substrate. It can be seen that, large number of platy particles exists. Some of the plates are in the micron range in size, in the long dimension. From these images it is hard to determine the thickness of the particles which is a critical factor in reaching the ultimate performance of any filler. The particle size range of the synthesized material has been analyzed by the Nanosight instrument and SEM. The first is by light scattering utilizing Nanosight instrument which yielded an average particle size around 400 nm. This result was also confirmed by SEM measurements. EDAX analysis indicates the existence of

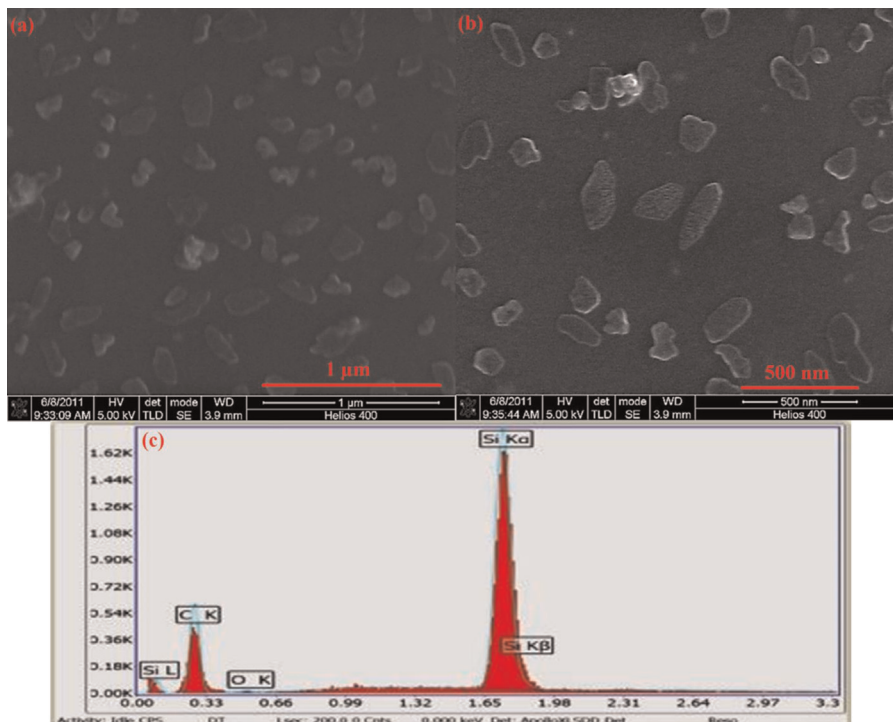


Fig. 1. SEM images of nanoparticles from the hydrogenation of humic acid derived from leonardite, (inset) EDAX analysis.

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